Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Vacancy and Interstitial Oxide Ion Migration in Heavily Doped $La_{2-x}Sr_xCoO_{4\pm\delta}$

SUPPORTING INFORMATION

Table SI-1. Buckingham potential and shell model parameters.

	A /eV	***ρ*** /Å	***C*** /eV·Å^6	***Y*** /e	***K*** /eV·Å^{-2}
La^{3+}-O^{2-} [this study, modified from 1]	1655.30	0.359	0	-0.25	750
Sr^{2+}-O^{2-} [2]	1400	0.35	0	1.33	21.43
Co^{3+}-O^{2-} [1]	1329.82	0.3087	0	2.04	196.3
O^{2-}—O^{2-} [1]	22764.3	0.149	43	-2.239	42

1.Cherry M., Islam M.S., Catlow C.R.A., *J. Solid State Chem.*, 118, (1995), 125.
2. Lewis G.V., Catlow C.R.A., *J. Phys.C: Solid state Phys.*, 18, (1985), 1149.

Table SI-2. Experimental and calculated lattice parameters and bond lengths for $LaSrCoO_4$ in space group 1.

parameter	**Exp /Å**	**Calc /Å**	**Δ(Exp-Calc) /Å**
a	3.802	3.833	-0.031
c	12.493	12.532	-0.039
La-O_{2ap}	2.441	2.422	0.019
La-O_{1eq}	2.582	2.576	0.006
La-O_{2eq}	2.707	2.717	-0.010
Co-O_{1eq}	1.901	1.923	-0.022
Co-O_{2ap}	2.059	2.062	-0.003

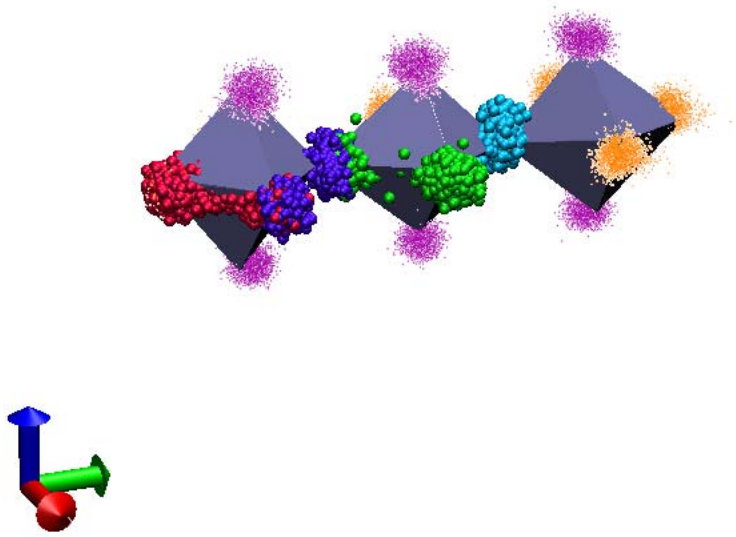

Figure SI-1 3D representation of a frequent migration event in $La_{0.8}Sr_{1.2}CoO_{3.95}$ involving five equatorial oxygen positions. Each oxygen involved in the migration event is represented by a different colour; spheres of the same colour indicate the positions occupied by a specific atom over the simulation time.

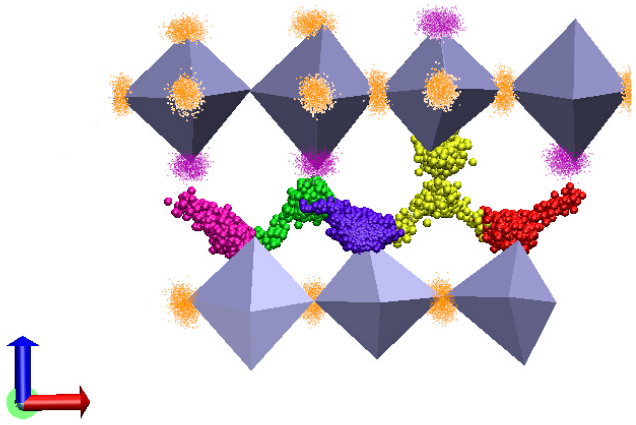

Figure SI-2 3D representation of oxygen interstitial migration in $La_{1.2}Sr_{0.8}CoO_{4.05}$. La and Sr ions have been omitted for clarity. Each oxygen involved in the migration event is represented by a different color. Spheres of the same color indicate the positions occupied by a specific atom over the simulation time.

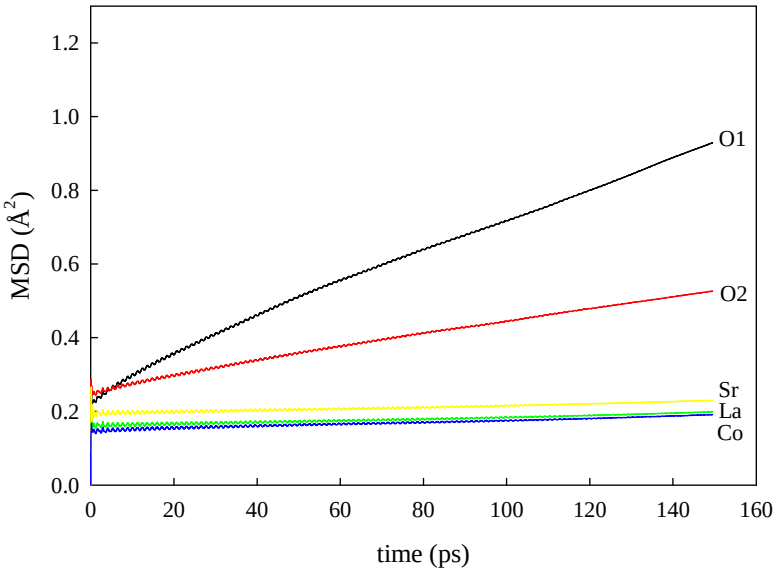

Figure SI-3 Example of mean square displacement parameters (MSD) as a function of time for $La_{0.8}Sr_{1.2}CoO_{3.9}$ – MD run at 1773K.

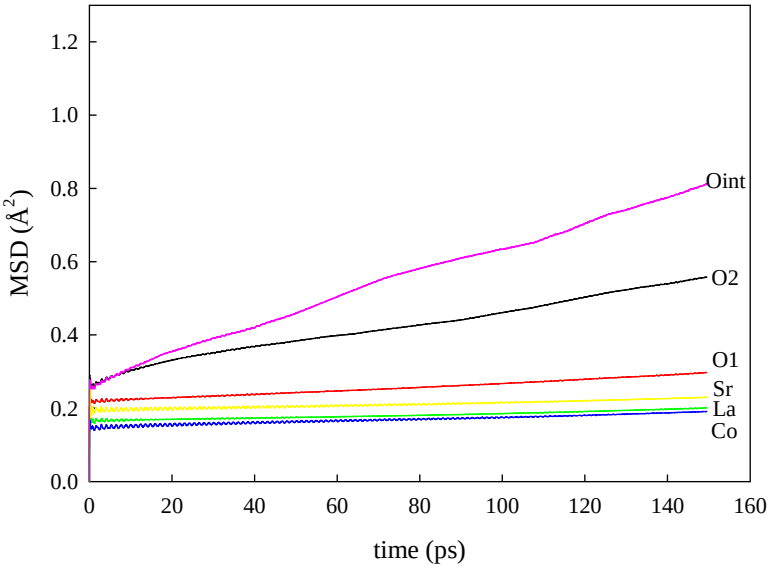

Figure SI-4 Example of mean square displacement parameters (MSD) as a function of time for $La_{1.2}Sr_{0.8}CoO_{4.1}$ – MD run at 1773K.

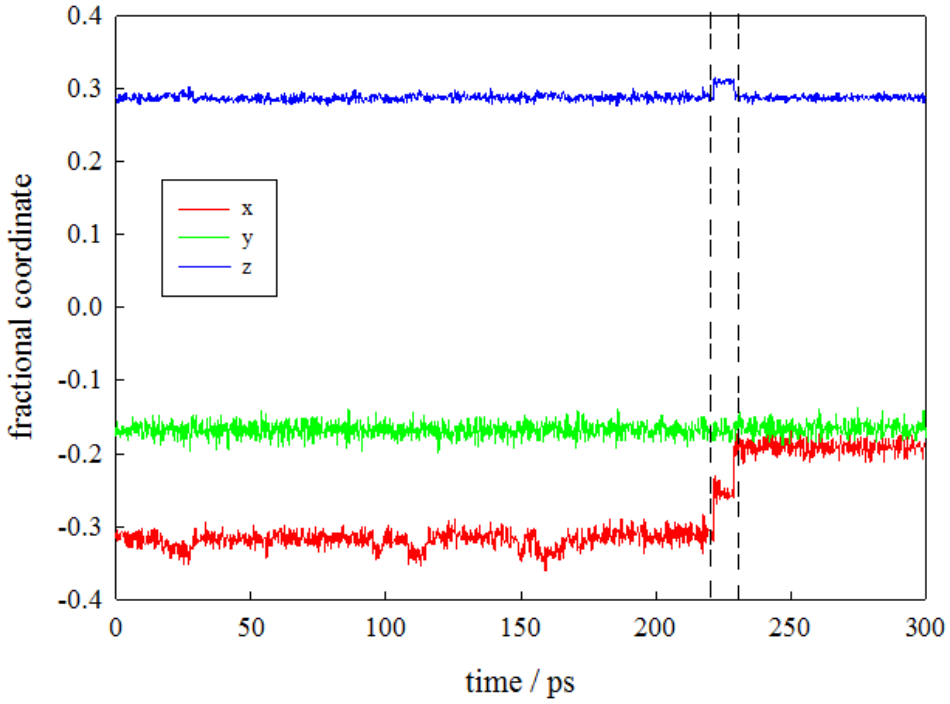

Figure SI-5 Example of atomic coordinates as a function of time for an O2-type atom in $La_{1.2}Sr_{0.8}CoO_{4.1}$ (MD run at 1773K), showing that the oxygen atom has a longer residence time close to the starting (and final) O2 position compared to the interstitial position. Dotted lines indicate the migration from the initial O2 to the intermediate O3 and the final O2 positions.

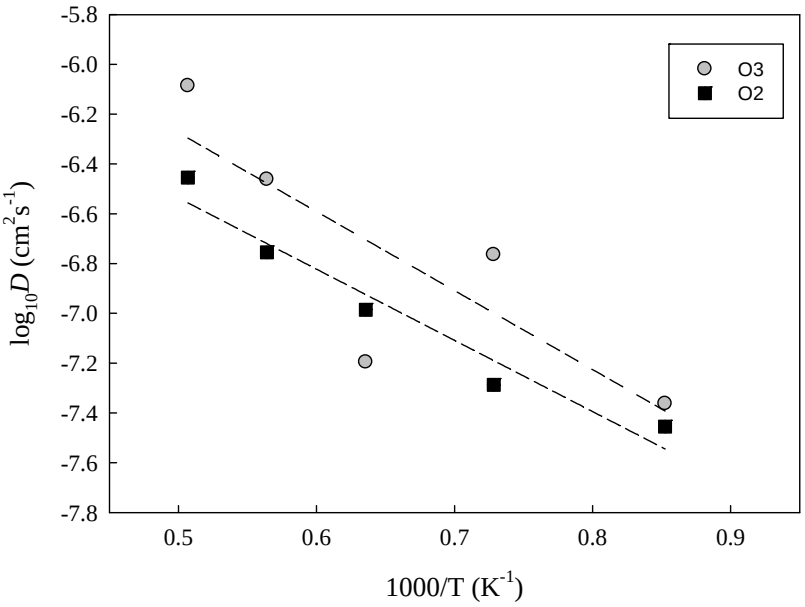

Figure SI-6. Arrhenius plots of the diffusion coefficients, D, for O3 (O_{int}) and O2. Despite of the data scattering, it is possible to state that the diffusion coefficients of O3 are higher than those of O2, but the activation energies are similar.